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Design and synthesis of new processible donor-acceptor dyad and triads

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Abstract

We report the design, synthesis and characterization of new processible well-defined donor (D)-acceptor (A) dyads and A-D-A triads for use in photovoltaic devices. The donor oligomers, which consist either of oligoaniline, thiophene-pyrrole-thiophene, phenyl-pyrrole-phenyl, or phenyl-thiophene-pyrrole-thiophene-phenyl segments, were covalently attached to fullerene C₆₀ which acts as an acceptor. All compounds were fully characterized using different analytical techniques.

Keywords: Transition-metal catalyzed reactions, Fullerene derivatives, Conjugated oligomers, UV-vis-NIR absorption, Solar cells

1. Introduction

The observation of photoinduced electron transfer between π -conjugated polymers as a donor (D) and fullerene C₆₀ as an acceptor (A) [1] has led to a number of detailed investigations of these composites. Although the photoinduced processes, which include the rate of forward and back electron transfer, the metastable characteristics of the charge-separated state created by photoinduced electron transfer reactions at the bulk heterojunction formed at the D-A interface, the mobility and the lifetime of the photogenerated charge carriers, the macroscopic ordering and its influence on these processes have been investigated in recent years, a comprehensive understanding on these phenomena is yet to be developed.

Along this line, D-A dyads and A-D-A triads consisting of well defined oligomer segments, which can be considered as a short chain counterpart of the polymers, covalently bound to fullerene C₆₀, are important model systems to gain insight in the rather complicated π -conjugated polymer-C₆₀ blend. Various dyads and triads have been synthesized and investigated in which oligothiophenes [2], oligo(*p*-phenylene vinylene)s [3,4], oligo(thienylene vinylene)s [5], or a substituted aniline [6], are covalently bound to C₆₀. While these dyads/triads can be treated as isolated molecules in solution, where intramolecular processes are dominant, the intermolecular interactions become important in the solid state [2]. It has been found that the creation of the photoinduced charge-separated state strongly depends on the polarity of solvent in which the dyad/triad is dissolved and such behavior can be accounted for by the Weller equation for the free energy change upon charge separation [2,4,6].

It is envisaged that use of donor segments consisting of either pyrrole/aniline may extend the lifetime of charge-separated state, since polypyrrole/polyanilines possess a lower oxidation potential in comparison to polythiophene/poly(phenylene vinylene)s. With this goal, we have designed a number of oligoaniline and pyrrole containing dyad and triads (Fig. 1). The synthesis and characterization of these well-defined molecules is presented.

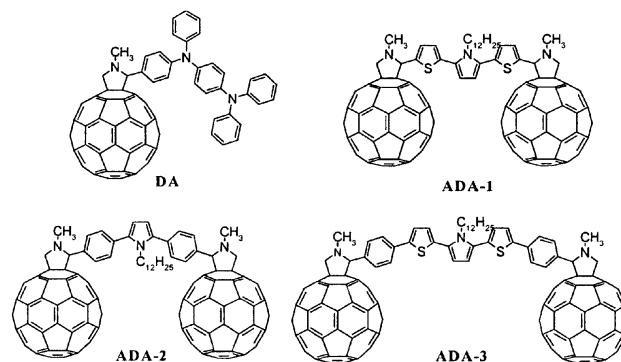


Fig. 1. Structures of different dyad and triads

2. Results and Discussion

The general strategy used in the synthesis of the dyad and triads depicted in Fig. 1, is to synthesize a conjugated oligomer, having one or two aldehyde functional groups (Fig. 2). These aldehydes are then coupled to C₆₀ by the Prato reaction [7].

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2.1 Synthesis of DA

N,N,N'-triphenylbenzene diamine (**1**) was prepared according to literature in 25% yield and purified by column chromatography using a mixture of *n*-hexane and ethyl acetate (9:1) as eluent [8]. Next, **1** was reacted with 4-bromobenzaldehyde in the presence of $\text{Pd}_2(\text{dba})_3/\text{BINAP}$ as a catalyst and cesium carbonate as a base in toluene to afford aldehyde **2** in 40% yield. **DA** was obtained in 70% yield by the Prato reaction using **2** as the reacting aldehyde.

2.2 Synthesis of ADA-1

1,4-Bis(2'-thienyl)-1,4-butanedione was reacted with dodecylamine in benzene to obtain 2,5-bis(2'-thienyl)pyrrole (**3**) [9]. Subsequent double α -formylation was achieved via a Vilsmeier-Haack reaction. Reaction of dialdehyde **4** with C_{60} was carried out under similar conditions described for **DA**, to afford **ADA-1** in 46% yield after the purification.

2.3 Synthesis of ADA-2

N-dodecyl-2,5-bis(trimethylstannyl)pyrrole (**5**) was obtained by α,α' -bisstannylation of *N*-dodecylpyrrole and subsequently reacted with 4-bromobenzaldehyde under Stille coupling conditions [10] to afford **6** in 75% yield. Reaction of dialdehyde **6** with C_{60} was carried out under similar conditions described for **DA**, to afford **ADA-2** in 45% yield after the purification.

2.4 Synthesis of ADA-3

N-dodecyl-2,5-bis(2'-(5'-trimethylstannyl)thienyl)pyrrole (**7**) was obtained under similar conditions as those employed for obtaining **4**, using trimethyltin chloride instead of dimethylformamide. Subsequent reaction of **7** with 4-bromobenzaldehyde under Stille coupling conditions [10] gave **8** in 60% yield, which was coupled to C_{60} under similar conditions described for **DA**, to give **ADA-3** in 41% yield.

3. Conclusions

The synthesis of new DA dyad and ADA triads is described. The materials were fully characterized by a number of analytical techniques. Photophysical and device characterization of these dyad and triads is currently underway and will be reported separately.

4. Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer at frequencies of 400.1 and 100.6 MHz with CDCl_3 (δ , ppm) as solvent and TMS as an internal standard or with a Varian Unity Plus (500 MHz) instrument using CS_2 as solvent and with a D_2O insert which acts as an external lock for ^1H reference ($\delta = 4.67$ ppm relative to the TMS scale) and CS_2 as internal ^{13}C reference ($\delta = 192.3$

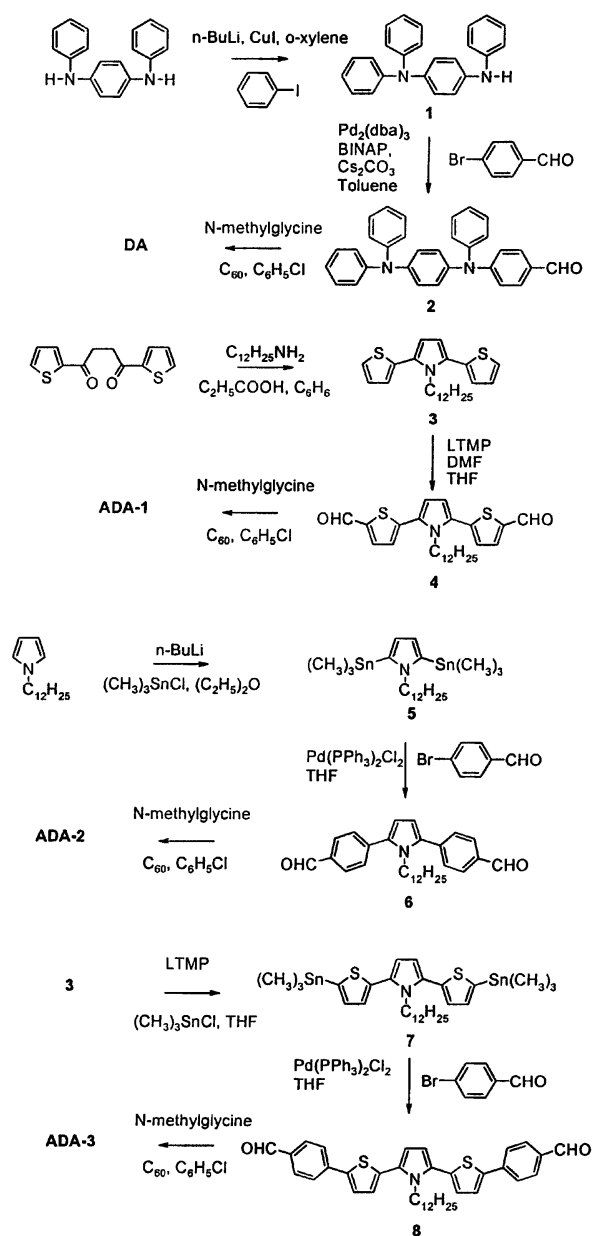


Fig. 2. Synthesis of dyad and triads depicted in Fig. 1

ppm relative to the TMS scale). All HPLC analyses were performed using an analytical Cosmosil Buckyprep[®] column (4.6 x 250 mm). MALDI-TOF-MS measurements were performed on a Micromass ToFSpec E[®] apparatus (positive-ion reflector mode) by using elemental sulfur as a matrix and CS_2 as a solvent [11].

***N*-(4'-Formylphenyl)-*N,N,N'*-triphenylbenzene diamine (**2**).** *N,N,N'*-triphenylbenzene diamine (**1**) was reacted with 4-bromobenzaldehyde (2 mol equiv) in the presence of 1 mol% of tris(dibenzylideneacetone)-dipalladium(0), 3 mol% of (*R*)-(+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, 1.5 mol equiv of cesium carbonate in toluene, for 2 days at 100 °C to give **2** in 40% yield. GC-MS (M.W. = 440 g/mol); $m/z = 440$ g/mol; ^1H NMR (δ , CDCl_3): 9.81 (s, 1H, -CHO), 7.67 (d, 2H, Ar-H),

6.95–7.27 (m, 21H, Ar-H); ^{13}C NMR (δ , CDCl_3): 190.7 (–CHO), 147.8, 145.4, 140.4, 131.8, 131.4, 130.1, 129.7, 129.4, 127.6, 127.5, 126.6, 125.4, 124.7, 124.6, 123.3, 118.9 (Ar-C).

DA. A solution of **2** (0.25 mmol), finely ground sarcosine (2 mmol), and C_{60} (1 mmol) in chlorobenzene (130 mL) was stirred and refluxed under dry nitrogen for 18 h. At the completion of reaction, the mixture was cooled to room temperature and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel, using CS_2 and a mixture of CS_2 -toluene (85:15) as eluents to afford **DA** in 70% yield. HPLC analysis (toluene/cyclohexane 75/25, $\lambda = 360$ nm, flow: 1 mL/min): single peak at $t_r = 5.1$ min. UV-Vis (1,2-dichlorobenzene, $\lambda_{\text{max}}(\epsilon)$): 323 (72790), 432 (4380), 706 (410). ^1H NMR (δ , CS_2 , 500 MHz): 7.74 (br. s, 2H, Ar-H), 6.96–7.36 (m, 21H, Ar-H), 5.08 (d, $J = 9.3$ Hz, 1H, NCHH), 5.02 (s, 1H, NCH), 4.40 (d, $J = 9.3$ Hz, 1H, NCHH), 2.99 (s, –NCH₃); ^{13}C NMR (CS_2 , δ , 125 MHz): 156.06, 153.67, 153.29, 153.26, 147.68, 147.28, 147.09, 147.08, 147.02, 146.59, 146.28, 146.18, 146.11, 146.07, 146.03, 145.98, 145.93, 145.91, 145.75, 145.58, 145.45, 145.34, 145.30, 145.21, 145.11, 145.08, 145.06, 145.00, 144.95, 144.52, 144.20, 142.99, 142.94, 142.86, 142.52, 142.46, 142.42, 142.12, 142.08, 141.99, 141.95, 141.92, 141.87, 141.86, 141.81, 141.66, 141.50, 141.44, 140.06, 140.00, 139.86, 139.15, 136.62, 136.49, 135.66, 135.63, 129.97, 129.86 (br.), 129.26, 129.19, 125.64, 125.02, 124.07, 123.77, 122.95, 122.59, 82.93, 77.26, 69.88, 68.67, 39.95.

2,5-Bis(2'-thienyl)pyrrole (3). was prepared by reacting 1,4-bis(2-thienyl)-1,4-butanedione, which is obtained from the reaction of 2-thiophene aldehyde with 3-dimethylamino-1-(2-thienyl)-propanone in dry DMF, with dodecylamine in benzene in the presence of 1 mol equiv of propionic acid under nitrogen, in 90% yield [9]. GC-MS (M.W. = 399 g/mol); $m/z = 399$ g/mol; ^1H NMR (δ , CDCl_3): 7.33 (dd, 2H, Th-H₅), 7.12 (bd, 4H, Th-H_{3,4}), 6.39 (s, 2H, Py-H), 4.18 (t, 2H, N-CH₂), 1.62 (m, 2H, N-CH₂-CH₂), 1.2–1.4 (m, 18H, –(CH₂)₉–), 0.95 (t, 3H, –CH₃); ^{13}C NMR (δ , CDCl_3): 134.9, 127.3, 126.1, 125.4 (Th-C), 128.3, 110.9 (Py-C), 45.6 (N-CH₂), 32.2 (N-CH₂-CH₂), 31.4, 29.9, 29.88, 29.80, 29.7, 29.6, 29.2, 26.7, 22.9 (–(CH₂)₉–), 14.4 (–CH₃).

2,5-Bis(2'-(5'-formylthienyl))pyrrole (4). To an ice-cooled mixture of **3** (0.01 mol) and 2,2,6,6-tetramethylpiperidine (0.025 mol) in dry THF was added *n*-butyllithium (1.6 M, 0.025 mol) under argon with stirring. After stirring at that temperature, the mixture was cooled to –70 °C and a solution of DMF (0.025 mol) in dry THF was added dropwise. After stirring the whole mixture at that temperature for an hour, it was slowly brought up to room temperature and stirred at that temperature for another 1 h. The reaction mixture was then added to a mixture of water and diethyl ether and the aqueous phase was extracted three times with diethyl ether and the combined diethyl ether fractions were dried (MgSO_4), filtered, and concentrated to afford a dark yellow viscous oil. Subsequent purification by

column chromatography (silica gel, CH_2Cl_2 as eluent) resulted in pure **4** in 80% yield. GC-MS (M.W. = 455); $m/z = 455$ g/mol. ^1H NMR (δ , CDCl_3): 9.88 (s, 2H, –CHO), 7.73 (d, 2H, $J = 4.0$ Hz, Th-H₄), 7.19 (d, 2H, $J = 4.0$ Hz, Th-H₃), 6.53 (s, 2H, Py-H), 4.32 (t, 2H, N-CH₂), 1.62 (m, 2H, N-CH₂-CH₂), 1.2–1.35 (m, 18H, –(CH₂)₉–), 0.86 (t, 3H, –CH₃).

ADA-1. Reaction of dialdehyde **4** with C_{60} was carried out under similar conditions described for **DA**, to give **ADA-1** in 46% yield after the purification by column chromatography (silica gel, CS_2 and a mixture of CS_2 /toluene (90:10) as eluents). HPLC (toluene, $\lambda = 360$ nm, flow: 1 mL/min): single peak at $t_r = 8.5$ min. UV-Vis (1,2-dichlorobenzene, $\lambda_{\text{max}}(\epsilon)$): 313 (93380), 329 (94980), 432 (8560), 706 (740); ^1H NMR (CS_2 , δ , 500 MHz): 7.43 (d, $J = 3.4$ Hz, 2H, Th-H), 7.02 (d, $J = 3.4$ Hz, 2H, Th-H), 6.34 (s, 2H, Py-H), 5.36 (s, 2H, –NCH), 5.09 (d, $J = 9.5$ Hz, 2H, –NCHH), 4.40 (d, $J = 9.5$ Hz, 2H, –NCHH), 4.07 (t, $J = 6.8$ Hz, 2H, NCH₂), 3.09 (s, 6H, –NCH₃), 0.92–1.50 (m, 20H, (CH₂)₁₀), 0.80 (t, 3H, –CH₃); ^{13}C NMR (CS_2 , δ , 125 MHz): 155.54, 153.46, 152.82, 152.70, 147.08, 147.05, 146.57, 146.10, 146.06, 146.03, 146.00, 145.97, 145.88, 145.73, 145.72, 145.48 (2), 145.42, 145.23, 145.21, 145.09, 145.05, 145.03, 145.01, 144.99, 144.93, 144.51, 144.37, 144.16, 144.11, 142.96, 142.82, 142.53, 142.42, 142.41, 142.39, 142.03, 141.97, 141.88, 141.85, 141.77, 141.76, 141.63, 141.60, 141.48, 141.40, 140.21, 140.19, 140.05, 140.01, 139.76, 139.30, 136.82, 136.81, 136.47, 136.25, 135.71, 135.43, 128.23, 127.78, 124.93, 111.44, 79.11, 76.95, 69.82, 68.40, 45.21, 40.25, 32.31, 31.20, 30.10, 30.04, 29.79, 29.69, 26.79, 23.35, 14.71. MALDI-TOF-MS: Calcd for $\text{C}_{150}\text{H}_{43}\text{N}_3\text{S}_2$: $m/z = 1949.3$, found: $m/z = 1949.4$ (M^+).

***N*-Dodecyl-2,5-bis(trimethylstannyl)pyrrole (5).** To an ice-cooled solution of *N*-dodecylpyrrole (0.08 mol) in dry diethyl ether, *n*-butyllithium (1.6 M, 60 mL) was added dropwise. At the end of addition, the reaction mixture was brought to room temperature and refluxed overnight. The reaction mixture was then cooled with an ice-salt mixture and a solution of trimethyltin chloride (0.16 mol) in dry diethyl ether was added dropwise, followed by stirring at room temperature for 1 h. The reaction mixture was subsequently diluted with diethyl ether, washed with water, dried over MgSO_4 and concentrated to get a red-colored viscous liquid. Subsequent distillation under reduced pressure resulted in **5** (bp. 153–5 °C/0.02 mbar) in 30% yield. ^1H NMR (δ , CDCl_3): 6.47 (s, 2H, Py-H_{3,4}), 3.90 (t, 2H, N-CH₂), 1.80 (m, 2H, N-CH₂-CH₂), 1.35 (m, 18H, –(CH₂)₉–), 0.90 (t, 3H, –CH₃) and 0.39 (s, 18H, –Sn(CH₃)₃); ^{13}C NMR (δ , CDCl_3): 136.30 (Py-C_{3,4}), 119.45 (Py-C_{2,5}), 53.60 (N-CH₂), 34.31, 32.22, 29.93, 29.84, 29.81, 29.77, 29.72, 29.66, 27.35, 23.01 (–CH₂–), 14.45 (–CH₃) and –7.97 (–Sn(CH₃)₃).

2,5-Bis(2'-(4'-formylphenyl))pyrrole (6). *N*-dodecyl-2,5-bis(trimethylstannyl)pyrrole (**5**) was reacted with 4-bromobenzaldehyde under Stille coupling conditions [10], in the presence of dichlorobis(triphenylphosphine)-palladium(II) in dry THF under argon to give **6** in 75%

yield. **6** was purified by column chromatography (silica gel, a mixture of *n*-hexane-CH₂Cl₂ (50:50) as eluent). GC-MS (M. Wt. 443 g/mol); *m/z* = 443 g/mol. ¹H NMR (δ, CDCl₃): 10.03 (s, 2H, -CHO), 7.94 (d, 4H, Phe-H₄), 7.62 (d, 4H, Phe-H₃), 6.41 (s, 2H, Py-H), 4.16 (t, 2H, N-CH₂), 1.2 (m, -(CH₂)₁₀-), 0.85 (t, 3H, -CH₃); ¹³C NMR (δ, CDCl₃): 191.9 (-CHO), 139.8, 137.5, 134.2, 130.2 (Phe-C), 135.0, 112.5 (Py-C), 46.2 (N-CH₂), 32.1, 29.7, 29.6, 29.5, 29.4, 28.9, 26.3, 26.1, 25.9, 22.9 (-CH₂-), 14.45 (-CH₃).

ADA-2. Reaction of dialdehyde **6** with C₆₀ was carried out under similar conditions as described for **DA**, to give **ADA-2** in 45% yield after the purification by column chromatography (silica gel, a mixture of CS₂/toluene (85:15) as eluent); HPLC (toluene, λ=360 nm, flow: 1 mL/min): single peak at 7.8 min. UV-Vis (1,2-dichlorobenzene, λ_{max}(ε)): 313 (98070), 327 (98950), 433 (8200), 706 (720). ¹H NMR (CS₂, δ, 500 MHz): 7.94 (br. s, 4H, 4PhH), 7.54 (br. d, *J* = 7.3 Hz, 4H, 4PhH), 6.26 (2xs, 2H, 2PyrrH), 5.13 (2xd, *J* = 9.3 Hz, 2H, 2NCHH), 5.11 (2xs, 2H, 2NCH), 4.45/4.44 (2xd, *J* = 9.3 Hz, 2H, 2NCHH), 4.01 (br. t, *J* = 7.1 Hz, 2H, NCH₂), 0.95–1.55 (m, 19H, 8CH₂ + CH₃), 0.87 (m, 2H, CH₂), 0.69 (m, 2H, CH₂). ¹³C NMR (CS₂, δ, 125 MHz): 155.88, 153.57, 153.00, 152.94, 147.05, 146.42, 146.19, 146.07, 146.02, 146.00, 145.96, 145.88, 145.72, 145.70, 145.48, 145.43, 145.31, 145.25, 145.20, 145.16, 145.08, 145.03, 144.99, 144.91, 144.90, 144.50, 144.34, 144.17, 144.12, 142.94, 142.83, 142.49, 142.39, 142.34, 142.06, 142.03, 141.96, 141.86, 141.83, 141.69, 141.49, 141.30, 140.06, 140.01, 139.74, 139.08, 136.63, 136.38, 135.70, 135.68, 135.55, 135.18, 134.21, 129.15 (br.), 128.86 (br.), 110.49, 83.07, 77.04, 69.91, 68.71, 45.23, 39.93, 32.31, 30.70, 30.07, 30.02, 29.91, 29.80, 29.34, 26.51, 23.35, 14.72. MALDI-TOF-MS: Calcd for C₁₅₄H₄₇N₃: *m/z* = 1937.4, found *m/z* = 1937.6 (M⁺).

N-Dodecyl-2,5-bis(2'-(5'-trimethylstannyl)thienyl)-pyrrole (7). **7** was obtained under similar conditions as described for obtaining **4** but using trimethyltin chloride instead of dimethylformamide. ¹H NMR (δ, CDCl₃): 7.17 (d, 2H, Th-H₃), 7.15 (d, 2H, Th-H₄), 6.32 (s, 2H, Py-H), 4.18 (t, 2H, N-CH₂), 1.2 (m, 20H, -(CH₂)₁₀-), 0.86 (t, 3H, -CH₃), 0.39 (s, 18H, -Sn(CH₃)₃). ¹³C NMR (δ, CDCl₃): 141.1, 137.6, 135.5, 126.9 (Th-C), 128.8, 110.6 (Py-C), 45.4, 32.2, 31.4, 29.9, 29.8, 29.6, 29.5, 29.1, 26.6, 22.9, 18.5 (-CH₂-), 14.4 (-CH₃), -7.8 (Sn(CH₃)₃).

N-Dodecyl-2,5-bis(2'-(5'-(4'-formylphenyl)thienyl)-pyrrole (8). **7** was reacted with 4-bromobenzaldehyde under Stille coupling conditions [10], in the presence of dichlorobis(triphenylphosphine)palladium(II) in dry THF under argon to give **8** in 60% yield. Purification of **8** was achieved by column chromatography (silica gel, a mixture of *n*-hexane-CH₂Cl₂ (25:75) as eluent). ¹H NMR (δ, CDCl₃): 9.99 (s, 2H, -CHO), 7.89 (d, 4H, *J* = 6.5 Hz, Phe-H), 7.75 (d, 4H, *J* = 6.5 Hz, Phe-H), 7.44 (d, 2H, *J* = 4.0 Hz, Th-H), 7.09 (d, 2H, *J* = 4.0 Hz, Th-H), 6.45 (s, 2H, Py-H), 4.27 (t, 2H, N-CH₂), 1.65 (m, N-CH₂-CH₂), 1.20 (m, 18H, -(CH₂)₉-), 0.86 (t, 3H, -CH₃); ¹³C NMR (δ, CDCl₃):

191.5 (-CHO), 142.0, 140.0, 126.9, 125.7 (Th-C), 136.7, 135.3, 130.7, 125.8 (Phe-C), 129.5, 111.9 (Py-C), 45.8 (N-CH₂), 32.1, 31.3, 29.9, 29.8, 29.7, 29.6, 29.5, 29.1, 26.6, 22.9 (-CH₂-), 14.4 (-CH₃).

ADA-3. Reaction of dialdehyde **8** with C₆₀ was carried out under similar conditions as described for **DA**, to get **ADA-3** in 41% yield after purification by column chromatography (silica gel, a mixture of CS₂/toluene (85:15) as eluent); HPLC (toluene, λ=360 nm, flow: 1 mL/min): single peak at *t*_r = 9.4 min. UV-Vis (1,2-dichlorobenzene, λ_{max}(ε)): 310 (sh. 95100), 329 (94760), 431 (sh. 25930), 705 (780). ¹H NMR (CS₂, δ, 500 MHz): 7.92 (s, br., 4H, Phe-H), 7.75 (d, br., *J* = 8.31 Hz, 4H, Ph-H), 7.36 (d, *J* = 3.4 Hz, 2H, Th-H), 7.06 (d, *J* = 3.4 Hz, 2H, Th-H), 6.38 (s, 2H, Py-H), 5.12 (d, *J* = 9.3 Hz, 2H, -NCHH), 5.09 (s, 2H, -NCH), 4.43 (d, *J* = 9.3 Hz, 2H, -NCHH), 4.31 (t, *J* = 7.8 Hz, 2H, -NCH₂), 2.99 (s, 6H, 2NCH₃), 1.75 (m, 2H, CH₂), 1.42 (m, 2H, CH₂), 1.28–1.40 (m, 16H, -(CH₂)₈-), 1.04 (t, *J* = 1.0 Hz, 3H, -CH₃). ¹³C NMR (CS₂, δ, 125 MHz): 155.84, 153.56, 153.00, 152.56, 147.07, 147.05, 146.42, 146.18, 146.11, 146.05, 146.01, 145.97, 145.95, 145.93, 145.89, 145.73, 145.53, 145.44, 145.39, 145.27, 145.21, 145.15, 145.09, 145.07, 145.03, 145.02, 144.95, 144.50, 144.45, 144.18, 144.17, 142.96, 142.84, 142.78, 142.51, 142.43, 142.40, 142.38, 142.08, 142.04, 141.96, 141.95, 141.89, 141.86, 141.85, 141.81, 141.72, 141.68, 141.50, 141.39, 140.07, 140.03, 139.86, 139.49, 136.74, 136.39, 135.97, 135.69, 135.55, 134.75, 134.19, 129.66 (br), 128.32, 126.03, 125.75 (br), 123.51, 111.72, 83.08, 76.97, 69.92, 68.75, 45.34, 39.96, 32.31, 31.50, 30.03, 29.95, 29.92, 29.79, 29.53, 26.86, 23.35, 14.70. MALDI-TOF-MS: Calcd for C₁₆₂H₅₁N₃S₂: *m/z* = 2101.4, found: *m/z* = 2101.2 (M⁺).

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